New Energy States of Atomic Hydrogen Formed in a Catalytic Helium-Hydrogen Plasma

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ABSTRACT

Extreme ultraviolet (EUV) spectroscopy was recorded on microwave discharges of helium with 2% hydrogen. Novel emission lines were observed with energies of $q \cdot 13.6\ eV$ where $q = 1,2,3,4,6,7,8,9,11$ or these lines inelastically scattered by helium wherein $21.2\ eV$ was absorbed in the excitation of $He\,(1s^2)$ to $He\,(1s^1 2p^1)$. The average hydrogen atom temperature was measured to be $180\text{-}210\ eV$ versus $\approx 3\ eV$ for pure hydrogen. The electron temperature T_e for helium-hydrogen was 28,000 K compared to 6800 K for pure helium. Known explanations for the novel series of spectral lines and extraordinary broadening were ruled out.

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1. Introduction

Suitable helium and hydrogen plasma light sources and spectrometers have been developed which permit observations in the vacuum ultraviolet (VUV). Developed sources that provide a suitable intensity are high voltage glow discharges, synchrotron devices, inductively coupled plasma generators, capacitively coupled RF discharges, and magnetically confined plasmas [1-4]. The basic spectral emission of pure helium and hydrogen light sources have been well known for about a century. The hydrogen spectrum is due to atomic hydrogen, molecular hydrogen, and hydrogen molecular ion [5-25]. Lykke et al. have measured the threshold for photodetachment of H^- at 6083 cm^{-1} [26]. And, recently, sources of H_3^+ have been developed and the corresponding spectrum has been recorded [27-28]. The helium spectrum is due to typically due to He and He^+ [5-6]. Helium excimers can be formed in atmospheric pressure, intense microhollow cathode discharges [29-30]. And, spectra of even more exotic possibilities such as He_2^+, and He_n have been obtained under special circumstances [31-32]. Spectra of helium-hydrogen mixtures may comprise the sum of the separate spectra with the additional possibility of emission from helium-hydrogen species. The only known additional species in a helium-hydrogen plasmas are HeH^+, HeH, HHe_2^+, and HHe_n^+ and He_n. Except for HeH^+, the formation of these species requires extremely specialized conditions such as extremely low temperatures [31-36]. We recorded EUV spectra of helium-hydrogen mixtures maintained in an Evenson cavity at room temperature and low pressures. Novel spectral lines in the short wavelength region (5-50 nm) were observed. Assignments to known species and contaminants were investigated and ruled out. The plasmas were further characterized by Balmer α and β line broadening and electron temperature measurements.

2. Experimental

EUV spectroscopy was recorded on microwave discharge plasmas of hydrogen, nitrogen, oxygen, carbon dioxide, helium, neon, argon, krypton, xenon, or 2% hydrogen mixed with each of these gases according to the methods given previously [37-38]. Each ultrapure gas alone or mixture was flowed through a half inch diameter quartz tube at 20 torr or 1 torr. The gas pressure to the cell was maintained by flowing the mixture while monitoring the pressure with a 10 torr and 1000 torr MKS Baratron absolute pressure gauge. The tube was fitted with an Opthos coaxial microwave cavity (Evenson cavity). The microwave generator was an Opthos model MPG-4M generator (Frequency: 2450 MHz). The input power to the plasma was set at 85 watts with forced air cooling of the cell. The spectrometer was a normal

incidence McPherson 0.2 meter monochromator (Model 302, Seya-Namioka type) equipped with a 1200 lines/mm holographic grating with a platinum coating. The wavelength region covered by the monochromator was $2-560\ nm$. The EUV spectrum was recorded with a channel electron multiplier (CEM) at $2500-3000\ V$. The wavelength resolution was about $0.02\ nm$ (FWHM) with an entrance and exit slit width of $50\ \mu m$. The increment was $0.2\ nm$ and the dwell time was $500.ms$ Novel peak positions were based on a calibration against the known He I and He II lines.

To achieve higher sensitivity at the shorter EUV wavelengths, the light emission from plasmas of helium alone, neon-hydrogen (98/2%), and argon-hydrogen (98/2%) were recorded with a McPherson 4° grazing incidence EUV spectrometer (Model 248/310G) equipped with a grating having 600 G/mm with a radius of curvature of $\approx 1\ m$. The angle of incidence was 87°. The wavelength region covered by the monochromator was $5-65\ nm$. The wavelength resolution was about $0.04\ nm$ (FWHM) with an entrance and exit slit width of $300\ \mu m$. A channel electron multiplier (CEM) at $2400\ V$ was used to detect the EUV light. The increment was $0.1\ nm$ and the dwell time was $1\ s$.

The widths of the 656.3 nm Balmer α and 486.1 nm Balmer β lines emitted from hydrogen or helium-hydrogen mixture (90/10)% microwave discharge plasmas were measured. The total pressure was 1 torr, and the input power to the plasma was set at 40 W. The plasma emission was fiber-optically coupled through a 220F matching fiber adapter positioned 2 cm from the cell wall to a high resolution visible spectrometer with a resolution of $\pm 0.006\ nm$ over the spectral range $190-860\ nm$. The spectrometer was a Jobin Yvon Horiba 1250 M with 2400 groves/mm ion-etched holographic diffraction grating. The entrance and exit slits were set to $20\ \mu m$. The spectrometer was scanned between $485.9-486.4\ nm$ and $655.5-657\ nm$ using a $0.005\ nm$ step size. The signal was recorded by a PMT with a stand alone high voltage power supply (950 V) and an acquisition controller. The data was obtained in a single accumulation with a 1 second integration time.

T_e was measured on microwave plasmas of helium alone and helium-hydrogen mixtures (90/10%) from the ratio of the intensity of the He 501.6 nm (upper quantum level n=3) line to that of the He 492.2 nm (n=4) line as described by Griem [39]. In each case, the total pressure was 0.1 torr. The visible spectrum ($400-560\ nm$) was recorded with the normal incidence EUV spectrometer with a photomultiplier tube (PMT) and a sodium salicylate scintillator. The PMT (Model R1527P, Hamamatsu) used has a spectral response in the range of $185-680\ nm$ with a peak efficiency at about $400\ nm$. The scan interval was $0.4\ nm$. The inlet and outlet slit were $300\ \mu m$ with a corresponding wavelength resolution of $2\ nm$. The spectra were repeated five times per experiment and were found to be reproducible within less than 5%.

The electron density was determined using a Langmuir probe according to the method given previously [40].

3. Results and discussion

A. EUV Spectroscopy

In the case of the EUV spectra of controls krypton, krypton-hydrogen (98/2%) mixture, xenon, xenon-hydrogen (98/2%) mixture, and hydrogen alone no peaks were observed below 77 nm, and no spurious peaks or artifacts due to the grating or the spectrometer were observed as shown for the spectrum of hydrogen alone in Figure 1. Only known He I and He II peaks were observed in the EUV spectrum of the control helium microwave discharge cell emission as shown in Figure 2.

The EUV spectra ($17.5-50$ nm) of the microwave cell emission of the helium-hydrogen mixture (98/2%) (top curve) and the helium control (bottom curve) are shown in Figure 2. Ordinary hydrogen has no emission in these regions. Novel peaks were observed at 45.6 nm, 37.4 nm, and 20.5 nm which do not correspond to helium. The peaks were very reproducible as shown in Figure 3.

The effect of decreasing the pressure from 20 torr to 1 torr was studied. At the 1 Torr condition, additional novel peaks were observed in the short wavelength region ($5-65$ nm) at 14.15 nm, 13.03 nm, 10.13 nm, and 8.29 nm which do not correspond to helium as shown in Figure 4. Known He I lines which were used for calibration of the novel peak positions were observed at 58.4 nm, 53.7 nm, and 52.4 nm. It is proposed that the 30.4 nm peak shown in Figures 2-4 was not entirely due to the He II transition. In the case of the helium-hydrogen mixture, the ratio of 30.4 nm (40.8 eV) peak to the 25.6 nm (48.3 eV) peak was 10 compared to 5.4 for helium alone as shown in Figure 2 which implies only a minor He II transition contribution to the 30.4 nm peak.

It is also proposed that the majority of the 91.2 nm peak not due to H^+ recombination. At 20 Torr, the ratio of the Lyman β peak to the 91.2 nm peak of the helium-hydrogen plasma was 2 compared to 8 for each control hydrogen and xenon-hydrogen plasma which indicates that the majority of the 91.2 nm peak was due to a transition other than the binding of an electron by a proton.

All known possibilities for the series of novel lines were considered. Spectra of species present in helium hydrogen mixtures and possible impurities were evaluated. The only known species in a helium-hydrogen plasmas are H^+, H_2^+, H_3^+, H^-, H, H_2, He_2^*, HeH^+, and remotely possibly HeH. Other exotic possibilities such as He_2^+, HHe_2^+, HHe_n^+ and He_n were

eliminated due to the extremely specialized conditions required for their formation such as extremely low temperatures that were unlike those in the helium-hydrogen microwave plasmas [31-32]. The impurities considered were nitrogen, oxygen, carbon dioxide, and water vapor from air, noble gas contaminants, silicon from the quartz tube, and contaminants from the vacuum system.

Regarding hydrogen species as a candidate of the series of novel lines, hydrogen alone has no known emission in this region ($< 77\ nm$) [5-25] as shown in Figure 1. This is a consequent of the binding energies of H, H_2, and H_2^+ being less than 16.3 eV [41-42], and the binding energy of H^- being only 0.75 eV [26]. The reaction to form H_3^+ is exothermic [43]

$$H_2^+ + H_2 \rightarrow H_3^+ + H + 1.7\ eV \tag{1}$$

From Eq. (1), the binding energy of H_3^+ can not be more than 22.43 eV, the sum of the binding energy of H_2^+, 16.25 eV (given by the sum of the bond energy of H_2^+, 2.651 eV [42], and the binding energy of H, 13.59844 eV [41]), the bond energy of H_2, 4.478 eV [42], and 1.7 eV. The corresponding emission is 55.3 nm which is outside of the region of the novel series observed in the region < 50 nm. Furthermore, H_3^+ possesses no excited electronic states, and consequently has no observable emission in the ultraviolet or visible regions [27]. H_3^+ can only be observed spectroscopically via vibration-rotational transitions which are in the infrared [27-28].

$He_2^{\bullet}$ emission is limited to the spectral region > 58.4 nm; thus, it was eliminated [29]. HeH^+ was eliminated since excited states of this ion were predicted to be unstable or only weakly bonding [33]. HeH emission was eliminated as the source of the series of novel peaks due to the extraordinarily low probability that HeH would form under the conditions of the helium-hydrogen microwave discharge. The existence of "bound" excited states of HeH has been shown by emission spectroscopy of HeH molecules produced by two ways: (1) by reactions of He and $H_2^{\bullet}$, and (2) in charge exchange collisions between HeH^+ and alkali vapors [34-35]. Conditions for either of these types of reactions were not present in the helium-hydrogen microwave plasmas. In addition, the known emission spectrum of HeH was not observed. In particular, HeH has broad emission peaks in the regions of 160-180 nm [36] and 200-400 nm [35] that were not observed in the helium-hydrogen plasmas, nor has the series of novel peaks been recorded on HeH emission. In addition, the novel series does not match the theoretical spectrum of attractive excited states that decay to a repulsive ground state. The theoretical emission of excited states belong to a Rydberg series that converges to the electronic ground state of the HeH^+ ion [34-35].

Air contaminants were also eliminated. Plasmas of nitrogen, oxygen, carbon dioxide, or these gases with 2% hydrogen showed no emission in the region < 50 nm as shown in Figure 5 for hydrogen mixed with nitrogen, oxygen, and carbon dioxide. In addition, water

vapor present in the oxygen-hydrogen plasma showed no emission in this region. Nitrogen was further eliminated since the intensity of the $N\,I\;{}^4S-{}^4P$ peaks of the nitrogen microwave plasma at 113.45 nm and 119.96 nm were 500,000 photons/s; whereas, these peaks were absent from the helium-hydrogen emission recorded with the same sensitivity. The spectrum of nitrogen matched that given in the literature [44] and NIST tables [5]. Similarly oxygen, carbon dioxide, and water vapor (oxygen-hydrogen mixture) were eliminated since O I peaks were observed from each plasma with intensities >100,000 photons/s; whereas, these peaks were absent from the helium-hydrogen emission recorded with the same sensitivity. The peaks that were absent from the helium-hydrogen microwave plasma, but were observed as intense peaks from the oxygen, carbon dioxide, and water vapor microwave plasmas were the O II peak at 83.45 nm and O I peaks at 87.79 nm, 93.5 nm, 99.1 nm, 103.92 nm, 104.09 nm, and 115.21 nm.

Emission of argon, krypton, and xenon as helium contaminants were eliminated. No emission was observed in the region <50 nm for xenon, xenon-hydrogen, krypton, and krypton-hydrogen as shown in Figure 6 for krypton or xenon mixed with hydrogen. In the case of the argon-hydrogen plasma, only known Ar II and III lines were observed at shorter wavelengths as shown in Figure 7. More significantly, the Ar I lines at 93.2 nm, 104.82 nm, and 106.66 nm have an intensities that are about three orders of magnitude that of the Ar II lines at 48.72 nm, 54.76, and 55.68 nm as observed in the argon control and from NIST tables [5]. This and other lines of argon in the region $50 - 560\ nm$ were not observed.

Neon has peaks at $45.635\ nm$ and $45.527\ nm$. To eliminate the possibility that the $45.6\ nm$ peak shown in Figures 2-4 was due to the presence of neon as an impurity, the EUV spectra ($25 - 50\ nm$) of the helium-hydrogen mixture (98/2%) (top curve) and control neon-hydrogen mixture (98/2%) (bottom curve) microwave discharge cell emission were recorded with a normal incidence EUV spectrometer and a CEM as shown in Figure 8. The novel lines were not observed in the neon-hydrogen control, and a series of Ne II lines were observed only in the control. The neon peaks at $45.635\ nm$ and $45.527\ nm$ were resolved in Figure 8; whereas, the $45.6\ nm$ peak in the helium-hydrogen plasma was about $3\ nm$ broad. Thus, it was not due to neon impurity. More significantly, the Ne I line at 73.58 nm has an intensity that is about three orders of magnitude that of the Ne II line at $45.635\ nm$ and $45.527\ nm$ as observed in the neon control and from NIST tables [5]. This and other lines of neon in the region $50 - 560\ nm$ were not observed.

Silicon from the quartz tube wall was eliminated since emission due to Si I, Si II, or Si III is not possible below 56 nm based on the NIST tables [5]. Emission from silicon was also eliminated since no silicon lines were observed in any spectrum in the 5-560 nm region. Using the same quartz tube run under identical conditions, no emission was observed in the region of

the novel series ($< 50\ nm$) in the case of the controls microwave discharge plasmas of hydrogen, nitrogen, oxygen, carbon dioxide, helium, krypton, xenon, or 2% hydrogen mixed with each of these gases.

Pump contaminants were eliminated. In order for pump contaminates to enter the region of the plasma, they must migrate against the pressure gradient of the differential pumping, $< 10^{-5}$ torr compared to 1 torr. This is highly unlikely. Furthermore, a turbo pump was used which does not have pump oil, and no impurities attributed to pumps were observed in any control spectrum in the 5-560 nm region.

The elimination of known explanations indicate a new result. Since the novel peaks were only observed with helium and hydrogen present, new hydrogen, helium, or helium-hydrogen species are possibilities. It is well known that empirically the excited energy states of atomic hydrogen are given by Rydberg equation (Eq. (2a) for $n > 1$ in Eq. (2b)).

$$E_n = -\frac{e^2}{n^2 8\pi\varepsilon_o a_H} = -\frac{13.598\ eV}{n^2} \tag{2a}$$

$$n = 1,2,3,\ldots \tag{2b}$$

The $n = 1$ state is the "ground" state for "pure" photon transitions (i.e. the $n = 1$ state can absorb a photon and go to an excited electronic state, but it cannot release a photon and go to a lower-energy electronic state). However, an electron transition from the ground state to a lower-energy state may be possible by a resonant nonradiative energy transfer such as multipole coupling or a resonant collision mechanism. Processes such as hydrogen molecular bond formation that occur without photons and that require collisions are common [45]. Also, some commercial phosphors are based on resonant nonradiative energy transfer involving multipole coupling [46].

We propose that atomic hydrogen may undergo a catalytic reaction with certain atoms and ions such as He^+ which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, $m \cdot 27.2\ eV$ wherein m is an integer. The theory was given previously [47]. The reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen that corresponds to a fractional principal quantum number. That is

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \ldots, \frac{1}{p}; \quad p \text{ is an integer} \tag{2c}$$

replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states. The $n = 1$ state of hydrogen and the $n = \frac{1}{\text{integer}}$ states of hydrogen are nonradiative, but a transition between two nonradiative states is possible via a nonradiative energy transfer, say $n = 1$ to $n = 1/2$. Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2\ eV$ (i.e. it resonantly accepts the nonradiative energy transfer from hydrogen atoms

and releases the energy to the surroundings to affect electronic transitions to fractional quantum energy levels). As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (2a) and (2c).

The novel peaks fit two empirical relationships. In order of energy, the set comprising the peaks at 91.2 nm, 45.6 nm, 30.4 nm, 13.03 nm, 10.13 nm, and 8.29 nm correspond to energies of $q \cdot 13.6\, eV$ where $q = 1,2,3,7,9,11$. In order of energy, the set comprising the peaks at 37.4 nm, 20.5 nm, and 14.15 nm correspond to energies of $q \cdot 13.6 - 21.21\, eV$ where $q = 4,6,8$. These lines can be explained as electronic transitions to fractional Rydberg states of atomic hydrogen given by Eqs. (2a) and (2c) wherein the catalytic system involves helium ions because the second ionization energy of helium is 54.417 eV, which is equivalent to $2 \cdot 27.2\, eV$. In this case, 54.417 eV is transferred nonradiatively from atomic hydrogen to He^{+} which is resonantly ionized. The electron decays to the $n = 1/3$ state with the further release of 54.417 eV which may be emitted as a photon. The catalysis reaction is

$$54.417\, eV + He^{+} + H[a_H] \rightarrow He^{2+} + e^{-} + H\left[\frac{a_H}{3}\right] + 108.8\, eV \tag{3}$$

$$He^{2+} + e^{-} \rightarrow He^{+} + 54.417\, eV \tag{4}$$

And, the overall reaction is

$$H[a_H] \rightarrow H\left[\frac{a_H}{3}\right] + 54.4\, eV + 54.4\, eV \tag{5}$$

Since the products of the catalysis reaction have binding energies of $m \cdot 27.2\, eV$, they may further serve as catalysts. Thus, further catalytic transitions may occur: $n = \frac{1}{3} \rightarrow \frac{1}{4}, \frac{1}{4} \rightarrow \frac{1}{5},$ and so on.

Electronic transitions to Rydberg states given by Eqs. (2a) and (2c) catalyzed by the resonant nonradiative transfer of $m \cdot 27.2\, eV$ would give rise to a series of emission lines of energies $q13.6\ \ eV$ where q is an integer. It is further proposed that the photons that arise from hydrogen transitions may undergo inelastic helium scattering. That is, the catalytic reaction

$$H[a_H] \xrightarrow{He^{+}} H\left[\frac{a_H}{3}\right] + 54.4\, eV + 54.4\, eV \tag{6}$$

yields 54.4 eV by Eq. (4) and a photon of 54.4 eV (22.8 nm). Once emitted, the photon may be absorbed or scattered. When this photon strikes $He\,(1s^2)$, 21.2 eV may be absorbed in the excitation to $He\,(1s^1 2p^1)$. This leaves a 33.19 eV (37.4 nm) photon peak and a 21.2 eV (58.4 nm) photon from $He\,(1s^1 2p^1)$. Thus, for helium the inelastic scattered peak of 54.4 eV photons from Eq. (3) is given by

$$E = 54.4\, eV - 21.21\, eV = 33.19\, eV\ (37.4\, nm) \tag{7}$$

A novel peak shown in Figures 2-4 was observed at 37.4 nm. Furthermore, the intensity of the 58.4 nm peak corresponding to the spectra shown in Figure 4 was about 60,000 photons/sec. Thus, the transition $He\,(1s^2) \rightarrow He\,(1s^1 2p^1)$ dominated the inelastic scattering of EUV peaks. The general reaction is

$$photon\ (h\nu) + He\,(1s^2) \rightarrow He\,(1s^1 2p^1) + photon\ (h\nu - 21.21\ eV) \qquad (8)$$

The two empirical series may be combined—one directly from Eqs. (2a, 2c) and the other indirectly with Eq. (8). The energies for the novel lines in order of energy are 13.6 eV, 27.2 eV, 40.8 eV, 54.4 eV, 81.6 eV, 95.2 eV, 108.8 eV, 122.4 eV and 149.6 eV. The corresponding peaks are 91.2 nm, 45.6 nm, 30.4 nm, 37.4 nm, 20.5 nm, 13.03 nm, 14.15 nm, 10.13 nm, and 8.29 nm, respectively. Thus, the identified novel lines correspond to energies of $q \cdot 13.6\,eV$ where $q = 1,2,3,4,6,7,8,9,11$ or these lines inelastically scattered by helium atoms wherein 21.2 eV was absorbed in the excitation of $He\,(1s^2)$ to $He\,(1s^1 2p^1)$. The values of q observed are consistent with those excepted based on Eq. (5) and the subsequent autocatalyzed reactions as discussed previously [48]. The broad satellite peak at 44.2 nm show in Figure 2-4 is consistent with the reaction mechanism of a nonradiative transfer to a catalyst followed by emission. There is remarkable agreement between the data and the proposed transitions to fractional Rydberg states and these lines inelastically scattered by helium according to Eq. (8). All other peaks could be assigned to He I, He II, second order lines, or atomic or molecular hydrogen emission. No known lines of helium or hydrogen explain the $q \cdot 13.6\ eV$ related set of peaks.

B. Line broadening and T_e measurements

The Doppler-broadened line shape for atomic hydrogen has been studied on many sources such as hollow cathode [49-50] and rf [51-52] discharges. The method of Videnovic et al. [49] was used to calculate the energetic hydrogen atom densities and energies from the widths of the 656.3 nm Balmer α and 486.1 nm Balmer β lines emitted from hydrogen or helium-hydrogen mixture (90/10)% microwave discharge plasmas. Gigosos et al. [53] have published a literature review of this method. The 486.1 nm Balmer β line widths recorded on a helium-hydrogen (90/10%) and a hydrogen microwave discharge plasma are shown in Figure 9. The average helium-hydrogen Doppler half-width of $0.52 \pm 5\%\ nm$ was not appreciably changed with pressure. The corresponding energy of 180 - 210 eV and the number densities of $5\,X\,10^{14} \pm 20\%\ atoms/cm^3$, depending on the pressure, were significant compared to only $\approx 3\ eV$ and $7\,X\,10^{13}$ $atoms/cm^3$ for pure hydrogen, even though 10 times more hydrogen was present. Only $\approx 3\,eV$ broadening was observed with xenon-hydrogen (90/10%) ruling out collisional broadening. Furthermore, only the hydrogen lines were broadened. The addition of

hydrogen to helium had no effect on the helium lines as shown for the 667.816 nm He I line in Figure 10.

Similarly, the average electron temperature for helium-hydrogen plasma was $28,000 \pm 5\%\ K$. Whereas, the corresponding temperature of helium alone was only $6800 \pm 5\%\ K$, and hydrogen alone was $5500 \pm 5\%\ K$. No high electric field was present in our experiments.

We have assumed that Doppler broadening due to thermal motion was the dominant source to the extent that other sources may be neglected. This assumption was confirmed when each source was considered. In general, the experimental profile is a convolution of two Doppler profiles, an instrumental profile, the natural (lifetime) profile, Stark profiles, Van der Waals profiles, a resonance profile, and fine structure. The contribution from each source was determined to be below the limit of detection [54-55].

Furthermore, no hydrogen species, H^+, H_2^+, H_3^+, H^-, H, or H_2, responds to the microwave field; rather, only the electrons respond. But, the measured electron temperature was about 1 eV; whereas, the measured H temperature was $180 - 210\ eV$. This requires that $T_H >>> T_e$. This result can not be explained by electron or external Stark broadening or electric field acceleration of charged species. The electron density was five orders of magnitude too low [54-55]. And, in microwave driven plasmas, there is no high electric field in a cathode fall region ($> 1\ kV/cm$) to accelerate positive ions as proposed previously [49-52] to explain significant broadening in hydrogen containing plasmas driven at a high voltage electrodes. It is impossible for H or any H-containing ion which may give rise to H to have a higher temperature than the electrons in a microwave plasma. The observation of excessive Balmer line broadening in a microwave driven plasma requires a source of energy other than that provided by the electric field. We propose that the source is the hydrogen catalysis reaction given by Eqs. (3-5) followed by subsequent reactions to further lower energy states given by Eqs. (2a, 2c).

4. Conclusion

We report that extreme ultraviolet (EUV) spectroscopy was recorded on microwave discharges of helium with 2% hydrogen. Novel emission lines were observed with energies of $q13.6\ \ eV$ where $q = 1,2,3,4,6,7,8,9,11$ or these lines inelastically scattered by helium atoms wherein $21.2\ eV$ was absorbed in the excitation of $He\,(1s^2)$ to $He\,(1s^1 2p^1)$. The authors could find no conventional explanation for the novel series of peaks and are open to suggestions. These lines matched transitions to fractional Rydberg states of atomic hydrogen

($n=\frac{1}{p}=\frac{1}{\text{integer}}$ replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states). An extremely high hydrogen-atom temperature of $180 - 210\ eV$ was observed with the presence of helium ion catalyst only with hydrogen present. Similarly, the average electron temperature for helium-hydrogen plasma was high, 28,000 K, compared to 6800 K for helium alone.

The novel emission lines and extraordinarily elevated temperatures may be explained by a highly energetic catalytic reaction involving a resonant nonradiative energy transfer of $m \cdot 27.2\ eV$ from atomic hydrogen to a catalyst wherein m is an integer. One such atomic catalytic system involves helium ions. The second ionization energy of helium is $54.4\ eV$; thus, the ionization reaction of He^{+} to He^{2+} has a net enthalpy of reaction of $54.4\ eV$ which is equivalent to $2 \cdot 27.2\ eV$. Since the products of the catalysis reaction have binding energies of $m \cdot 27.2\ eV$, they may further serve as catalysts.

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Figure Captions

Figure 1. The EUV spectrum (20-125 nm) of the control hydrogen microwave discharge cell emission that was recorded with a normal incidence EUV spectrometer and a CEM. No emission was observed below < 77 nm.

Figure 2. The EUV spectra ($17.5-50\ nm$) of the microwave cell emission of the helium-hydrogen mixture (98/2%) (top curve) recorded at 20 Torr with a normal incidence EUV spectrometer and a CEM, and control helium (bottom curve) recorded at 20 Torr with a 4° grazing incidence EUV spectrometer and a CEM. Only known He I and He II peaks were observed with the helium control. Reproducible novel emission lines were observed at 45.6 nm and 30.4 nm with energies of $q \cdot 13.6\ eV$ where $q = 2$ *or* 3 (Eqs. (2a, 2c)) and at 37.4 nm and 20.5 nm with energies of $q \cdot 13.6\ eV$ where $q = 4$ *or* 6 that were inelastically scattered by helium atoms wherein 21.2 eV was absorbed in the excitation of $He\ (1s^2)$ to $He\ (1s^1 2p^1)$ as proposed in Eq. (8).

Figure 3. TheE UV spectra ($17.5-50\ nm$) of the microwave cell emission of the helium-hydrogen mixture (98/2%) recorded at 20 Torr with a normal incidence EUV spectrometer and a CEM showing the reproducibly of the novel emission lines observed at 45.6 nm and 30.4 nm with energies of $q \cdot 13.6\ eV$ where $q = 2$ *or* 3 (Eqs. (2a, 2c)) and at 37.4 nm and 20.5 nm with energies of $q \cdot 13.6\ eV$ where $q = 4$ *or* 6 that were inelastically scattered by helium atoms wherein 21.2 eV was absorbed in the excitation of $He\ (1s^2)$ to $He\ (1s^1 2p^1)$ as proposed in Eq. (8).

Figure 4. The short wavelength EUV spectra ($5-50\ nm$) of the microwave cell emission of the helium-hydrogen mixture (98/2%) (top curve) and control hydrogen (bottom curve) recorded at 1 Torr with a normal incidence EUV spectrometer and a CEM. No hydrogen emission was observed in this region, and no instrument artifacts were observed. Reproducible novel emission lines were observed at 45.6 nm, 30.4 nm, 13.03 nm, 10.13 nm, and 8.29 nm with energies of $q \cdot 13.6\ eV$ where $q = 2,3,7,9,$ *or* 11 and at 37.4 nm, 20.5 nm, and 14.15 nm with energies of $q \cdot 13.6\ eV$ where $q = 4,6,$ *or* 8 that were inelastically scattered by helium atoms wherein 21.2 eV was absorbed in the excitation of $He\ (1s^2)$ to $He\ (1s^1 2p^1)$ as proposed in Eq. (8). The peak at 13.03 nm was observed as a weak shoulder on the 14.15 nm peak, and has been observed in repeated (non-presented) spectra.

Figure 5. The EUV spectra ($20-50\ nm$) of microwave discharge plasmas of mixtures of 2% hydrogen with nitrogen, oxygen, or carbon dioxide that were recorded with a normal incidence EUV spectrometer and a CEM. No peaks were observed in this region from any of the controls. The oxygen-hydrogen plasma also contained water vapor which showed no emission in this region.

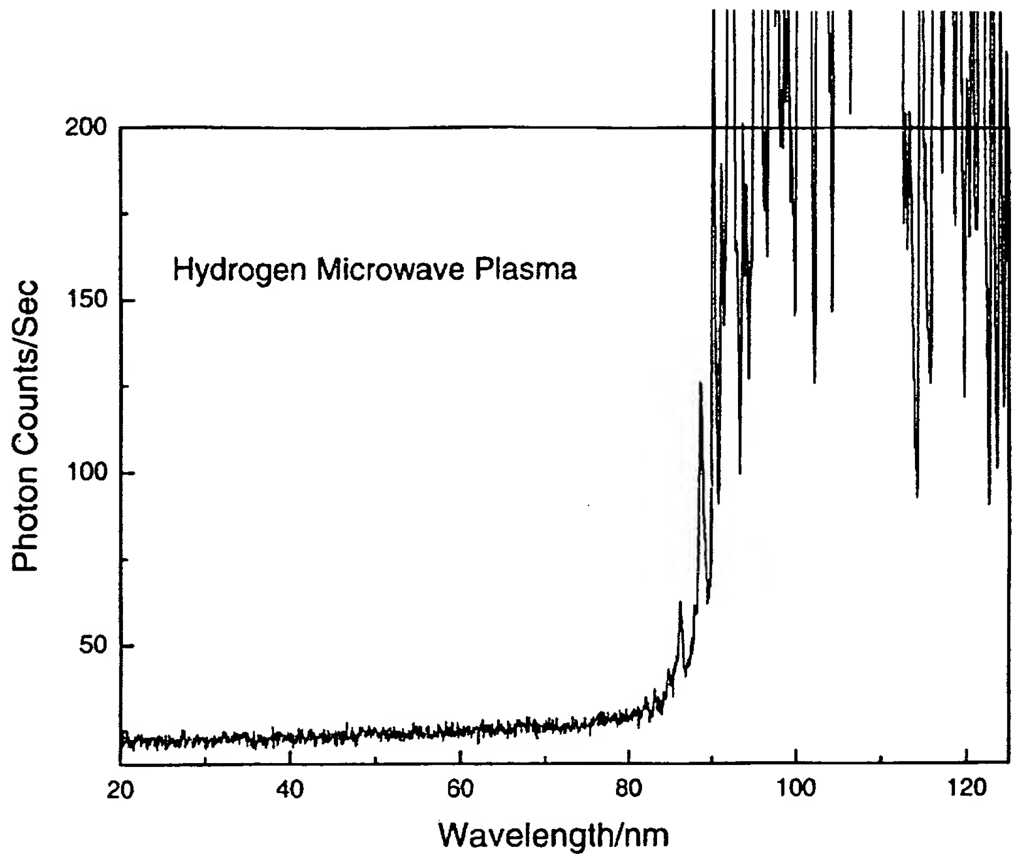
Figure 6. The EUV spectra ($20 - 50\ nm$) of the emission from control microwave discharge plasmas of hydrogen alone or 2 % hydrogen mixed with krypton or xenon that was recorded with a normal incidence EUV spectrometer and a CEM. No emission was observed in this region.

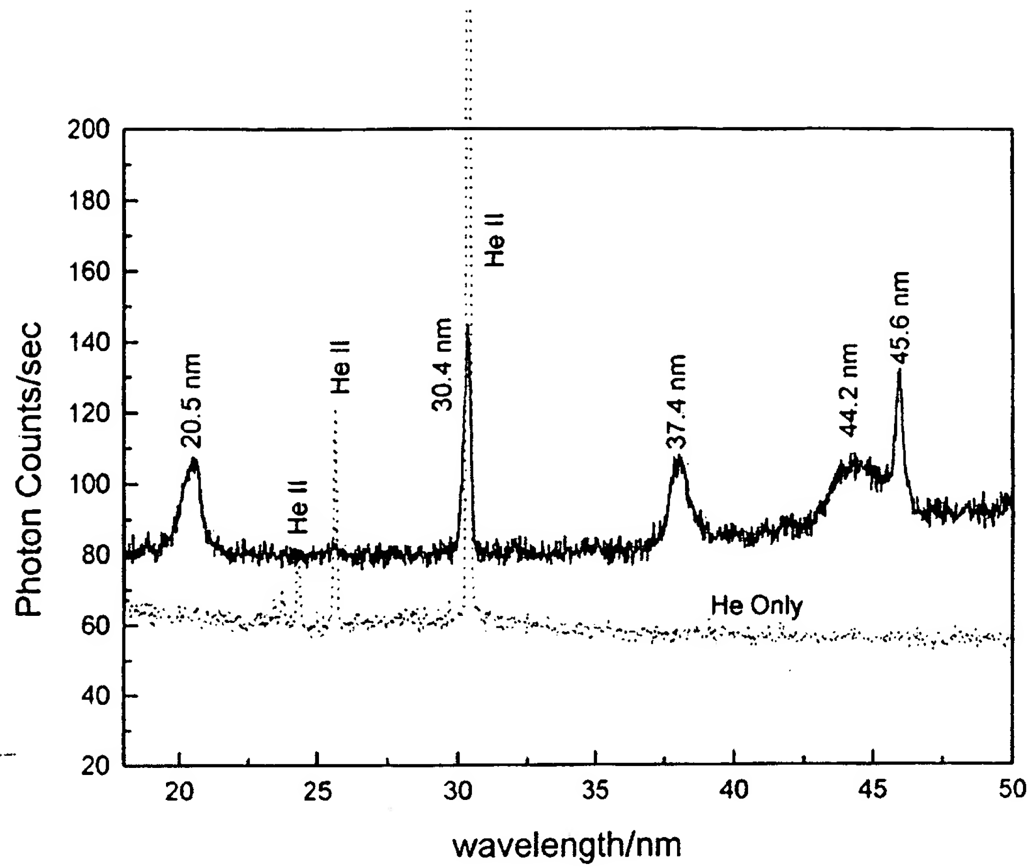
Figure 7. The EUV spectrum ($38 - 50\ nm$) of the control argon-hydrogen (98/2%) microwave discharge cell emission that was recorded with a 4° grazing incidence EUV spectrometer and a CEM. Only known Ar II and Ar III lines were observed.

Figure 8. The EUV spectra ($25 - 50\ nm$) of the helium-hydrogen mixture (98/2%) microwave discharge cell emission recorded with a normal incidence EUV spectrometer and a CEM (top curve) and control neon-hydrogen mixture (98/2%) (bottom curve) recorded with a 4° grazing incidence EUV spectrometer and a CEM. The spectra did not match based on wavelength and peak width. The novel peaks were not observed in the neon-hydrogen control, and a series of Ne II lines were observed only in the control.

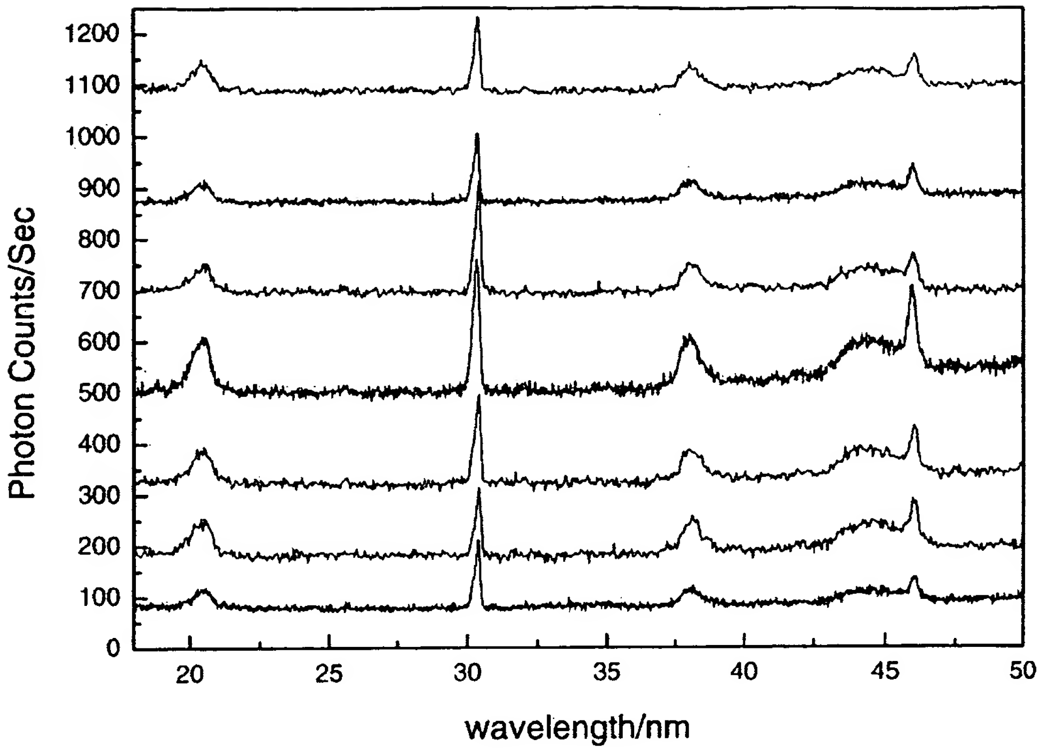
Figure 9. The 486.1 nm Balmer β line width recorded with a high resolution ($\pm 0.006\ nm$) visible spectrometer on helium-hydrogen (90/10%) and hydrogen microwave discharge plasmas. Significant broadening was observed from the helium-hydrogen plasma corresponding to an average hydrogen atom temperature of $180 - 210\ eV$ compared to $\approx 3\ eV$ for hydrogen alone.

Figure 10. The 667.816 nm He I line width recorded with a high resolution ($\pm 0.006\ nm$) visible spectrometer on helium-hydrogen (90/10%) and helium microwave discharge plasmas. No broadening was observed in either case.

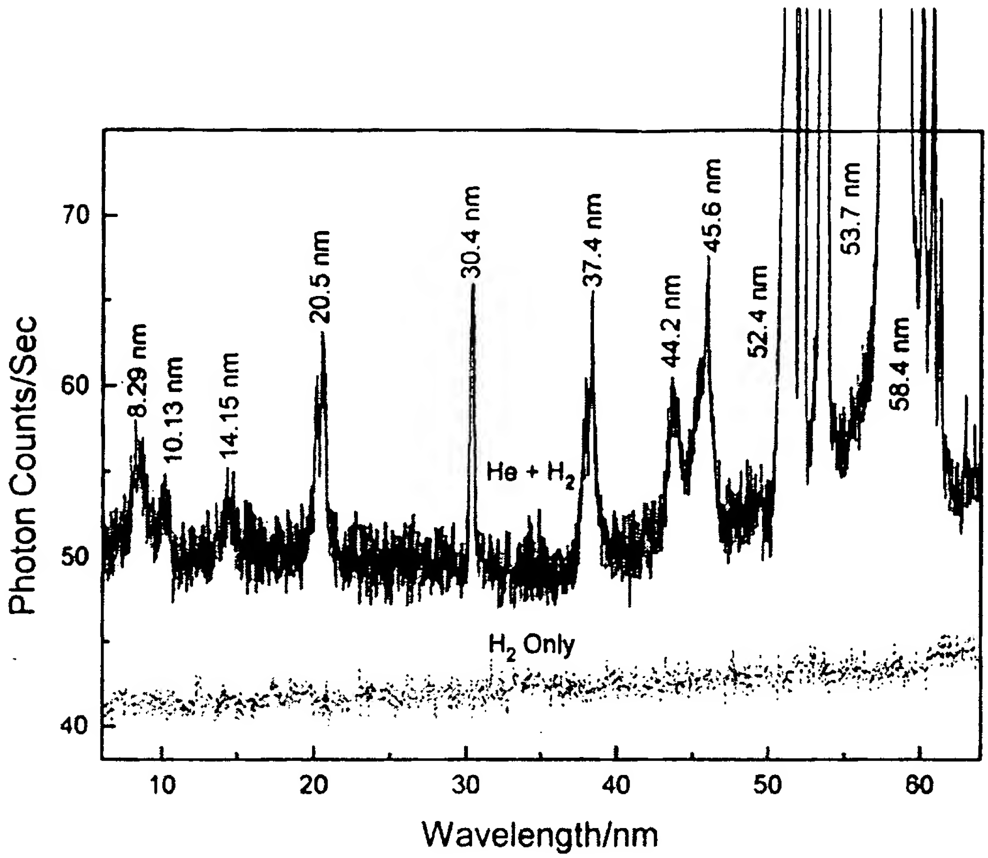

Hydrogen Microwave Plasma
Photon Counts/Sec
Wavelength/nm
200
150
100
50
20
40
60
80
100
120

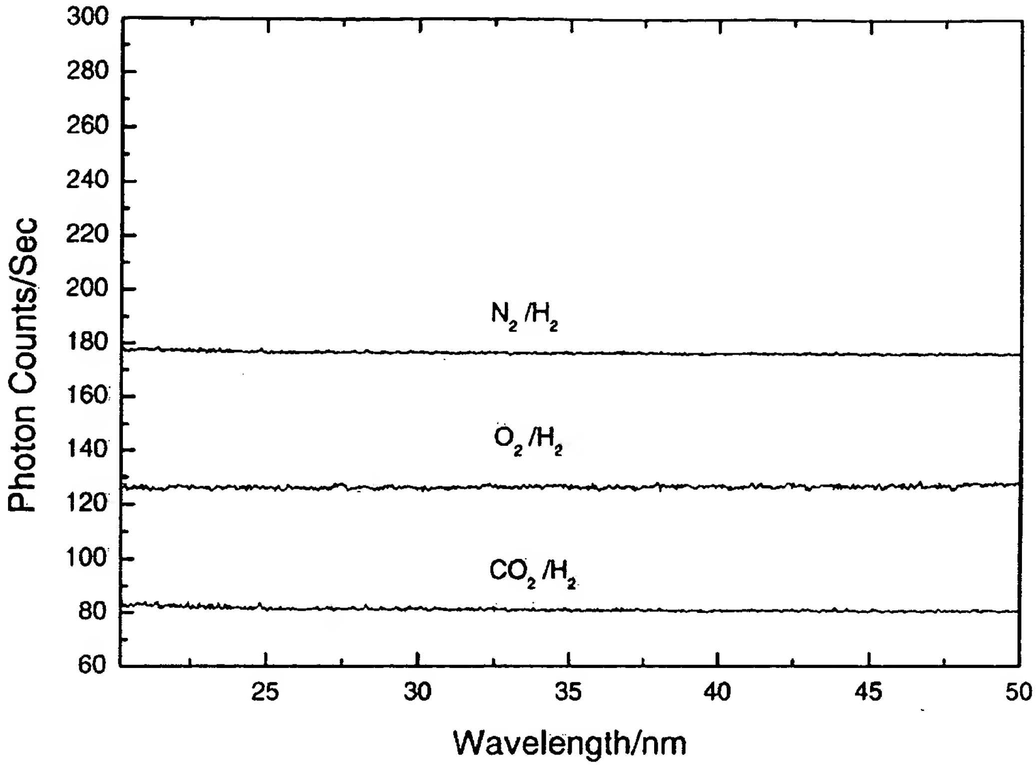


Photon Counts/sec
wavelength/nm
20.5 nm
He II
He II
30.4 nm
He II
37.4 nm
44.2 nm
45.6 nm
He Only

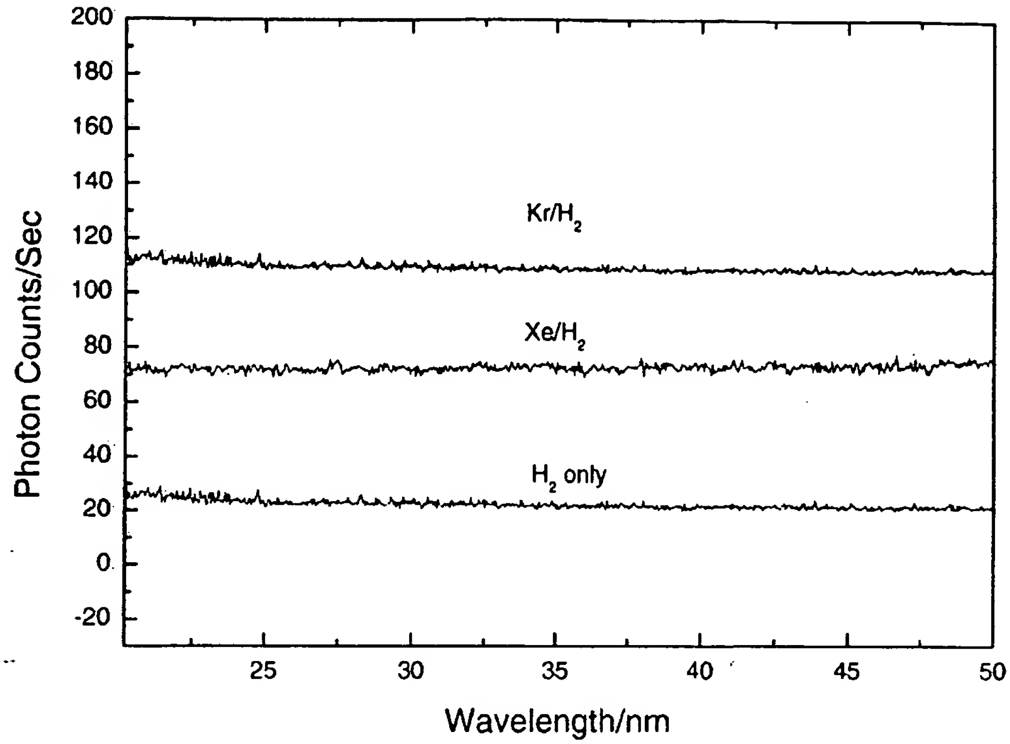


Photon Counts/Sec
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
20
25
30
35
40
45
50
wavelength/nm


8.29 nm
10.13 nm
14.15 nm
20.5 nm
30.4 nm
37.4 nm
44.2 nm
45.6 nm
52.4 nm
53.7 nm
58.4 nm
He + H_2
H_2 Only
Photon Counts/Sec
Wavelength/nm
40
50
60
70
10
20
30
40
50
60



Photon Counts/Sec
300
280
260
240
220
200
180
160
140
120
100
80
60
N2 /H2
O2 /H2
CO2 /H2
25
30
35
40
45
50
Wavelength/nm


Photon Counts/Sec
Wavelength/nm
Kr/H2
Xe/H2
H2 only
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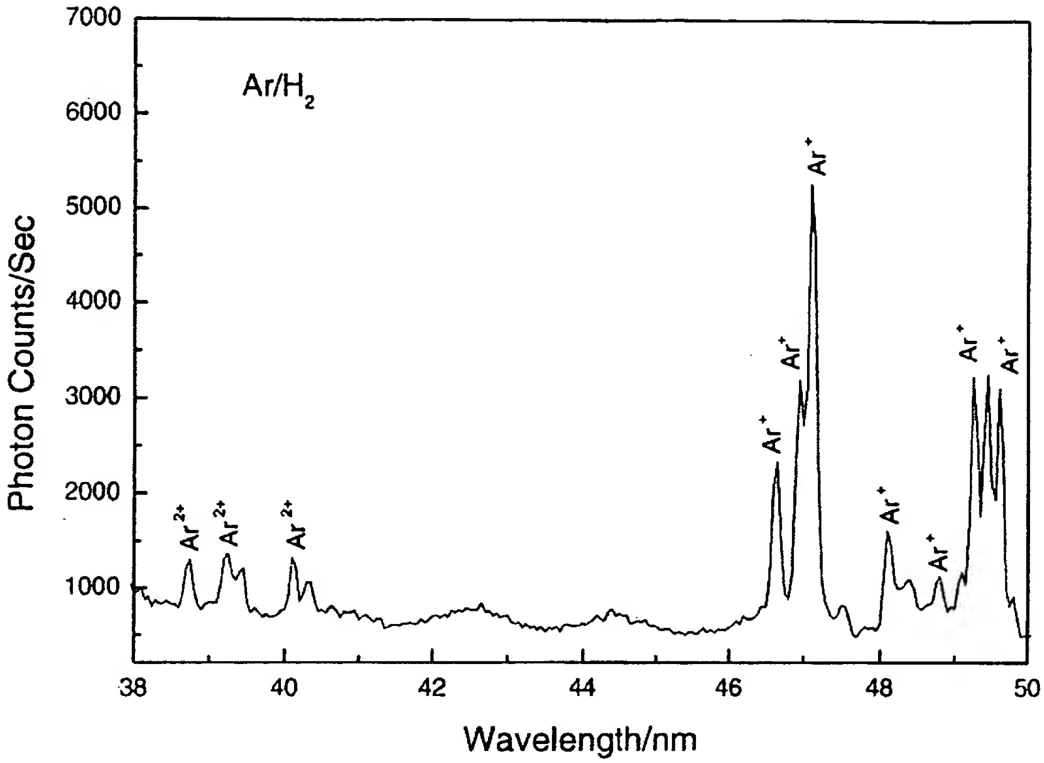
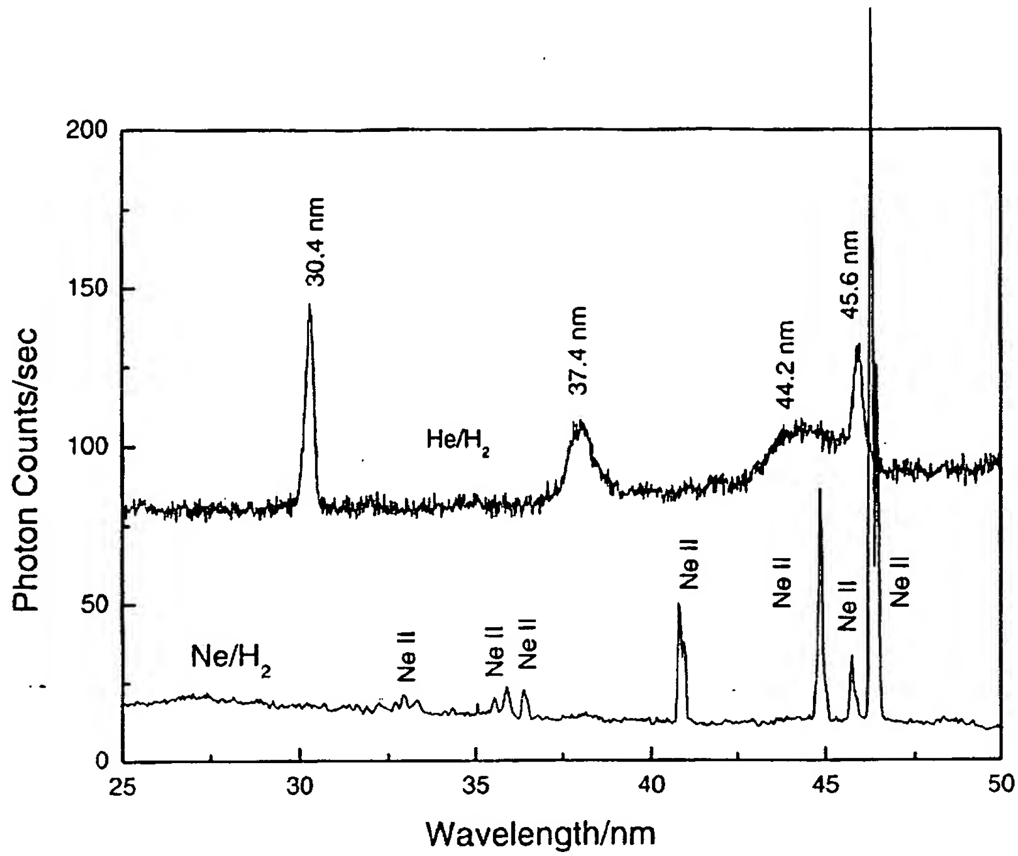
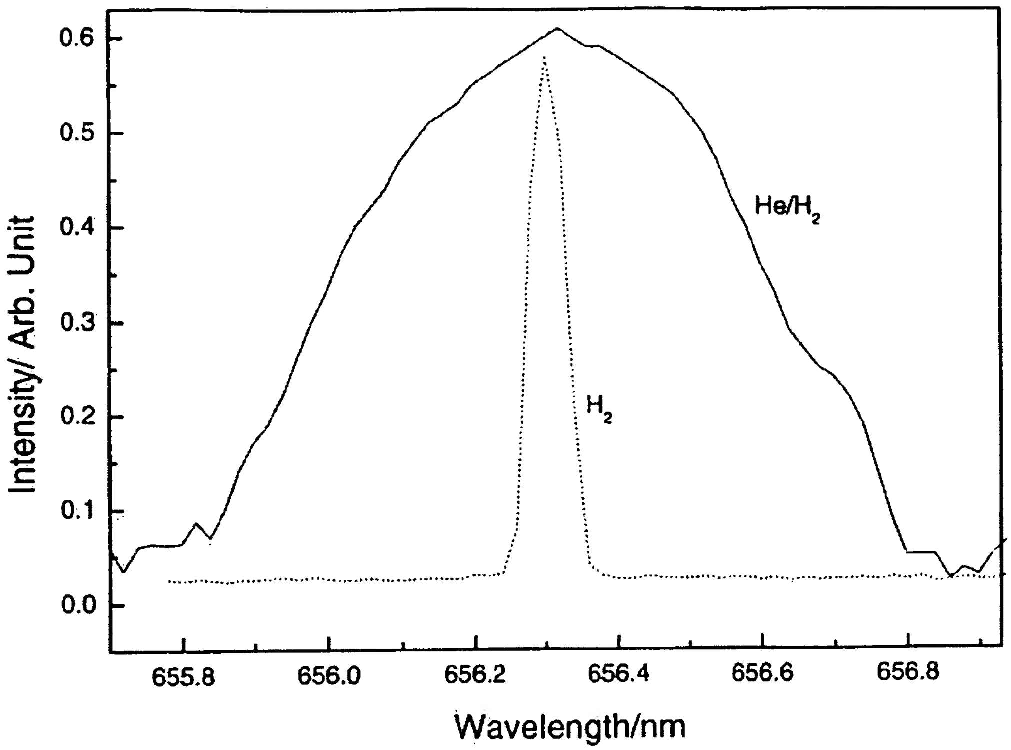
180
160
140
120
100
80
60
40
20
0
-20
25
30
35
40
45
50

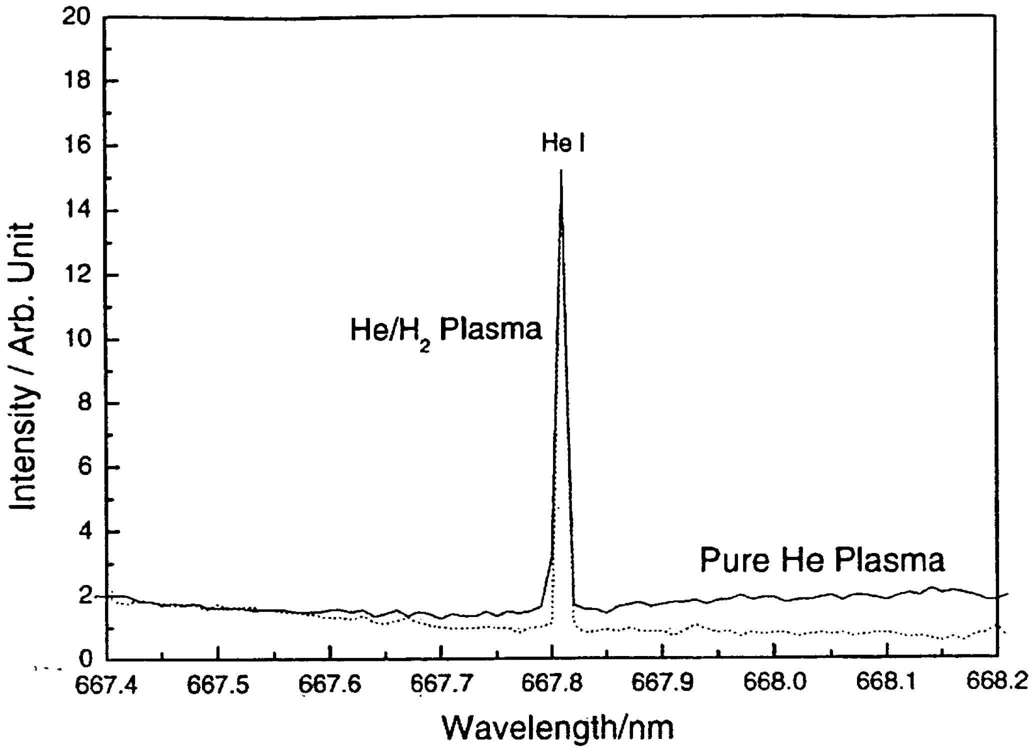

Ar/H$_2$
Photon Counts/Sec
Wavelength/nm
7000
6000
5000
4000
3000
2000
1000
38
40
42
44
46
48
50
Ar^{2+}
Ar^{2+}
Ar^{2+}
Ar$^+$
Ar$^+$
Ar$^+$
Ar$^+$
Ar$^+$
Ar$^+$
Ar$^+$



200
150
100
50
0
Photon Counts/sec
30.4 nm
37.4 nm
44.2 nm
45.6 nm
He/H_2
Ne/H_2
Ne II
Ne II
Ne II
Ne II
Ne II
Ne II
Ne II
25
30
35
40
45
50
Wavelength/nm



0.6
0.5
0.4
0.3
0.2
0.1
0.0
Intensity/ Arb. Unit
He/H2
H2
655.8
656.0
656.2
656.4
656.6
656.8
Wavelength/nm



He I
He/H_2 Plasma
Pure He Plasma
Intensity / Arb. Unit
Wavelength/nm
0
2
4
6
8
10
12
14
16
18
20
667.4
667.5
667.6
667.7
667.8
667.9
668.0
668.1
668.2

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